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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO) 11 May 2001

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2001-115**
Mario Fajardo and Michelle DeRose, "Status of Cryosolid Propellants Task"

AFOSR Molecular Dynamics Contractors' Meeting **(Statement A)**
(Irvine, CA, 21 May 01) (Deadline: 18 May 01)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
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____
PHILIP A. KESSEL Date
Technical Advisor
Space and Missile Propulsion Division

Status of CryoSolid Propellants Task

Mario E. Fajardo and Michelle E. DeRose

* Cryosolid Propellants Team
* HEDM Cryosolid Propellants Concept (Atoms in Solid Hydrogen)
* Cryosolid Propellants Payoffs, Objectives, Approach
* Requirement for Spectroscopic Diagnostics
* Rapid Vapor Deposition of Thick Parahydrogen (pH_2) Solids
* Update on Al/pH_2 and Mg/pH_2 Experiments
* Opportunities for Supporting In-House Effort
* Recommendations for Future Experiments
* Open Discussion

Cryosolid Propellants Team

* Mario E. Fajardo, Michelle E. DeRose, and Simon Tam
  Bill Larson and Jessica Harper (B atom source)

* J. Boatz, J. Mills, P. Langhoff, and J. Sheehy (in-house theory)

* FY00 Interactions with AFOSR Contractors:
  - P. Dagdigian @ Johns Hopkins: Al/H_2 & B/H_2 Complexes
  - M. Alexander @ U. Maryland: B/H_2 Interaction Potentials
  - G. Voth @ U. Utah: Path-Integral Monte Carlo Simulations
  - G. Scoles & K. Lehmann @ Princeton U.: Helium Clusters

* External Collaborators:
  - T. Momose @ Kyoto U.: High Resolution IR Spectroscopy

* Summer Visiting Professors:
  - R.J. Hinde @ U. Tennessee: Dopant-Induced IR Activity
  - D. Anderson @ U. Wyoming: Dopant IR Absorptions

"Revolutionary" vs. "Evolutionary" HEDM Concepts

* "Revolutionary" means better than LOX/LH_2:

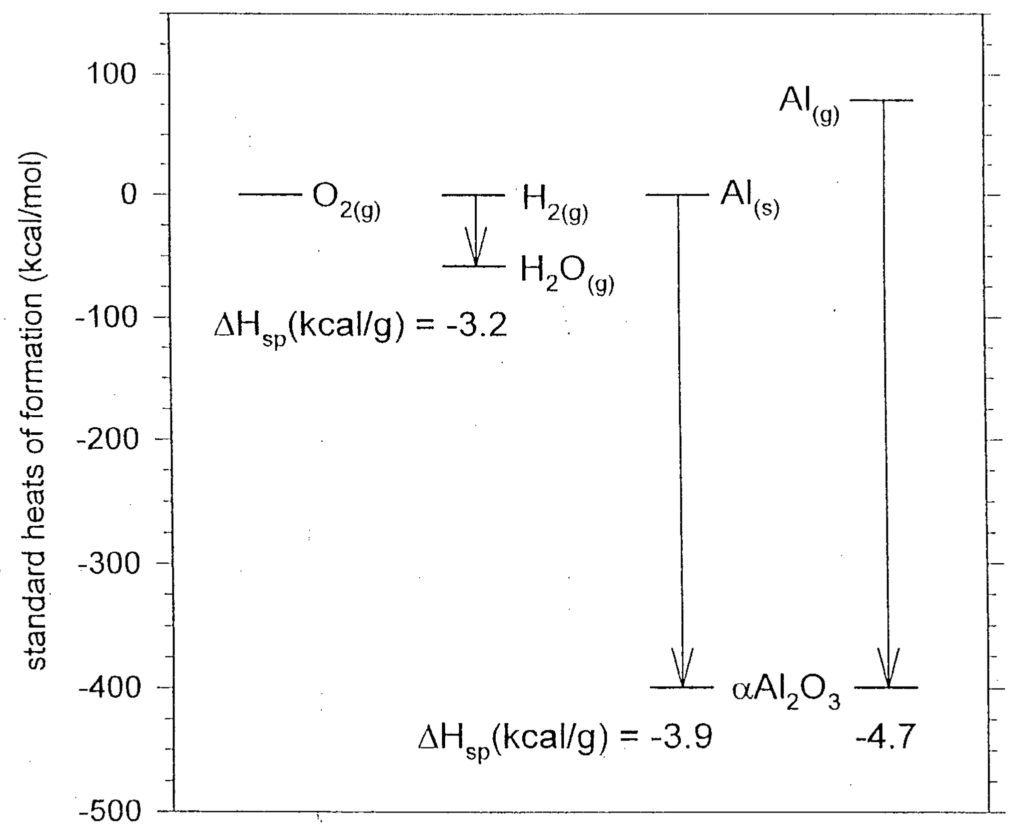
LOX/LH_2	$\Delta H_{sp} = 12.6$ MJ/kg (3.0 kcal/g)
HEDM Target:	$\Delta H_{sp} > 15.0$ MJ/kg (3.6 kcal/g)

* Early (c1990) Revolutionary HEDM Concepts:

- tetrahydrogen (H_4)
- metastable triplet helium (He* and He_2*)
- spin-polarized atomic hydrogen ($H\uparrow$)
- high-spin species (^5CO)
- dications (AB^{++}, ABC^{++})
- ♥ "non-metallics" (*e.g.* O_4/H_2, N_4, N_8, N_{20}) N_5^+!
- metallic hydrogen
- ♥ metal atoms and clusters in solid H_2

Cryosolid Propellants Concept

Use cryogenic solid hydrogen as a "packaging material" to store energetic species such as metal atoms and clusters.



Cryosolid Propellants Payoffs

Increased Specific Impulse

$$I_{sp} \propto \sqrt{\Delta H_{sp}}$$

LOX/LH_2 : $I_{sp} = 400$ s

5% B/sH_2 + LOX : $I_{sp} = 500$ s (+25%)*

5% Al/sH_2 + LOX: $I_{sp} = 450$ s (+12%)*

* calculated for $P_{chamber} = 1000$ PSIA, $P_{exhaust} = 14.7$ PSIA

Greater Propellant Density

liquid H_2 @ 20 K : $\rho = 0.070$ g/cm^3

solid H_2 @ 2 K : $\rho = 0.087$ g/cm^3 (+25%)

50/50 liquid He/solid H_2 : $\rho = 0.105$ g/cm^3 (+50%)

Atom Additive Payoffs (5 % molar)

Sea level specific impulse, I_{sp}, in seconds (% change)

$P_{chamber}$ = 1000 PSIA, $P_{exhaust}$ = 14.7 PSIA

Additive	in standard state $M(5\%)/LOX/H_2$	as atoms $M(5\%)/LOX/H_2$	monoprop. $M(5\%)/H_2$
none	403		
C	381 (-5%)	515 (+28%)	515 (+28%)
B	407 (+1%)	508 (+26%)	465 (+15%)
Be	427 (+6%)	493 (+22%)	
Si	400 (-1%)	460 (+14%)	
Al	407 (+1%)	454 (+13%)	
H	403	430 (+7%)	380 (-6%)
Li	404	428 (+6%)	
Mg	400 (-1%)	416 (+3%)	

Cryosolid Propellants Objectives

* <u>Make</u> solid hydrogen samples (any size) containing 5% molar concentration of trapped energetic additives.

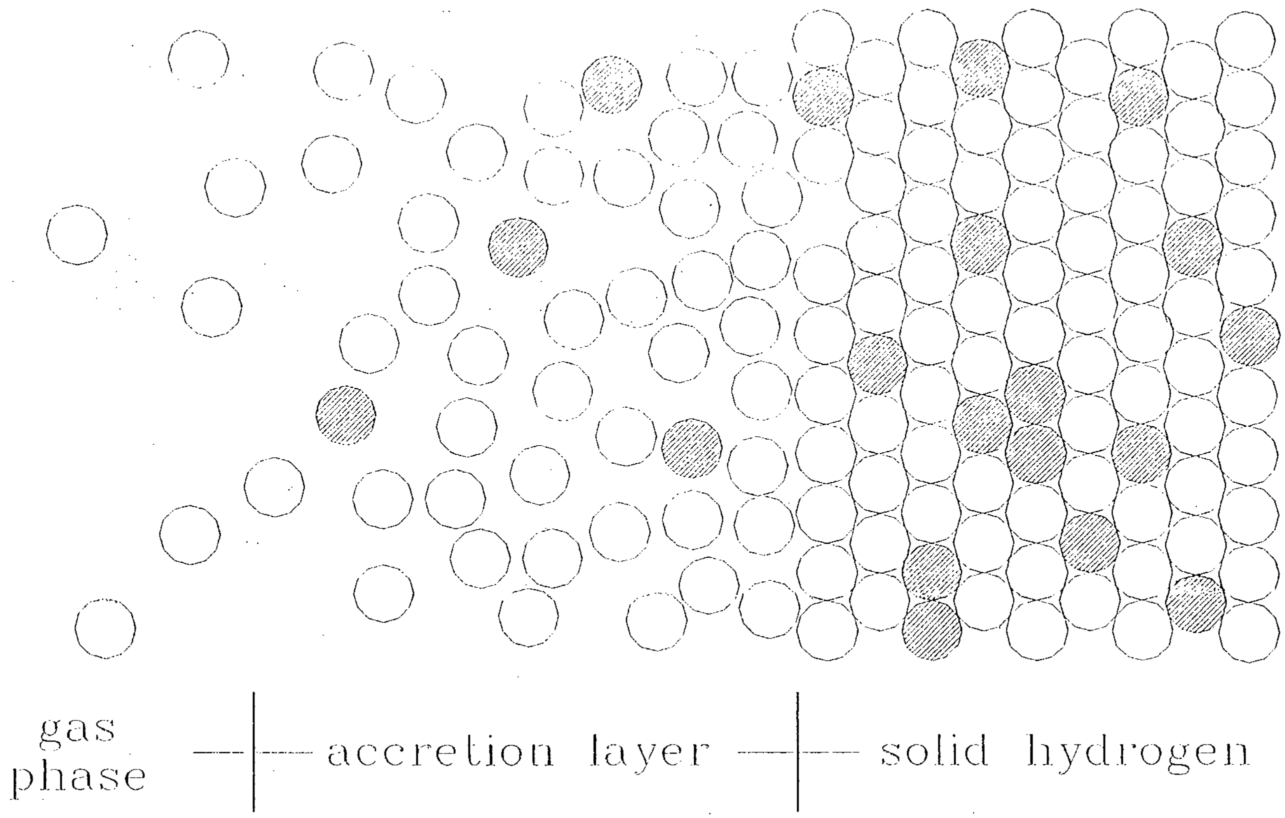
* <u>Measure</u> absolute concentrations of energetic species.

* <u>Scale-up</u> samples; produce ~ 1 cm^3 samples in our lab.

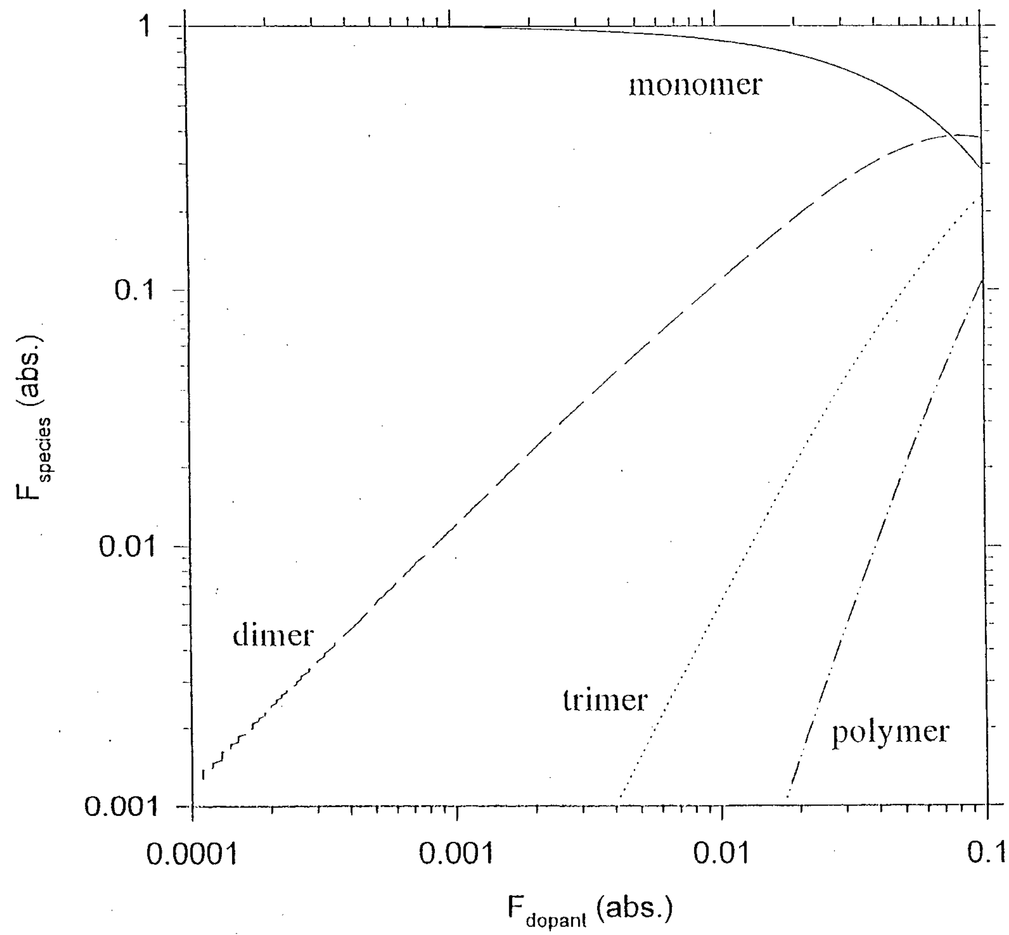
Example: 5% Al/pH_2, $V = 1\ cm^3$
assume each Al atom replaces one H_2 molecule
$\Rightarrow$ 58 mg Al / 83 mg H_2 (*see display item*)
$\therefore$ $\rho = 0.142\ g/cm^3$ (+100%)

Cryosolid Propellants Approach

* Rapid vapor deposition of metal atom vapor and pre-cooled parahydrogen gas onto a liquid helium cooled substrate in vacuum.



Recombination at High Concentrations



Bernoulli Trails (statistical) model of dopant agglomeration: $P(k,12) = \binom{12}{k} f^k (1-f)^{12-k}$

Requirement for Spectroscopic Diagnostics

* Develop spectroscopic techniques to identify and measure concentrations of trapped species.

* Beer's Law: $A = \sigma N d$

A = absorbance = $-\ln (I/I_0)$

σ = absorption cross-section

N = species number densities

d = pathlength

$N d$ = "column density"

* UV/vis absorption for low metal atom column densities.

* IR absorptions, direct and dopant-induced pH_2 transitions, for reaction products & metal atoms at large column densities.

The Perils of Calorimetry

108 GEORGE C. PIMENTEL

TABLE IX

CONCENTRATIONS OF FREE RADICALS REPORTED

Radical	Matrix	Mole per cent radicals	Method of production and estimate[a]	Reference
O	O_2	4–20	Gas, cal	Minkoff *et al.* (1959).
		<3	Gas, IR	Harvey and Bass (1958)
		~1	Gas, cal	Broida and Lutes (1956)
OH	$Ca(OH)_2$	0.6	γ, ESR	R. Livingston[b]
N	N_2	4	Gas, cal	Minkoff *et al.* (1959)
		0.2	Gas, cal	Broida and Lutes (1956)
		0.03	γ, ESR	Wall *et al.* (1959b)
		>0.03	Gas, cal	Fontana (1958)
		0.01–0.04	Gas, MS	Fontana[c]
OH(?)	HCOOH	0.2	γ, ESR	Matheson and Smaller (1955)
CH_3	CH_4	0.14	γ, ESR	Wall *et al.* (1959a)
H	CH_4	0.1	γ, ESR	Wall *et al.* (1959a)
N	NH_3	0.1	Gas, ESR	Cole and Harding (1958)
H	$HClO_4$—H_2O	0.1	γ, ESR	Livingston *et al.* (1955)
H	H_2O	0.01	γ, ESR	Matheson and Smaller (1955)
H, NH_2(?)	NH_3	0.01	γ, ESR	Matheson and Smaller (1955)
ROH	Alcohols	~0.01	UV, ESR	D. Ingram[b]
H	H_2	0.0006	γ, ESR	Wall *et al.* (1959a)

[a] Abbreviations: gas = rapid condensation of gaseous radicals; γ = gamma ray *in situ* production; UV = photolytic *in situ* production; IR = infrared analysis; cal = calorimetry; MS = magnetic susceptibility.

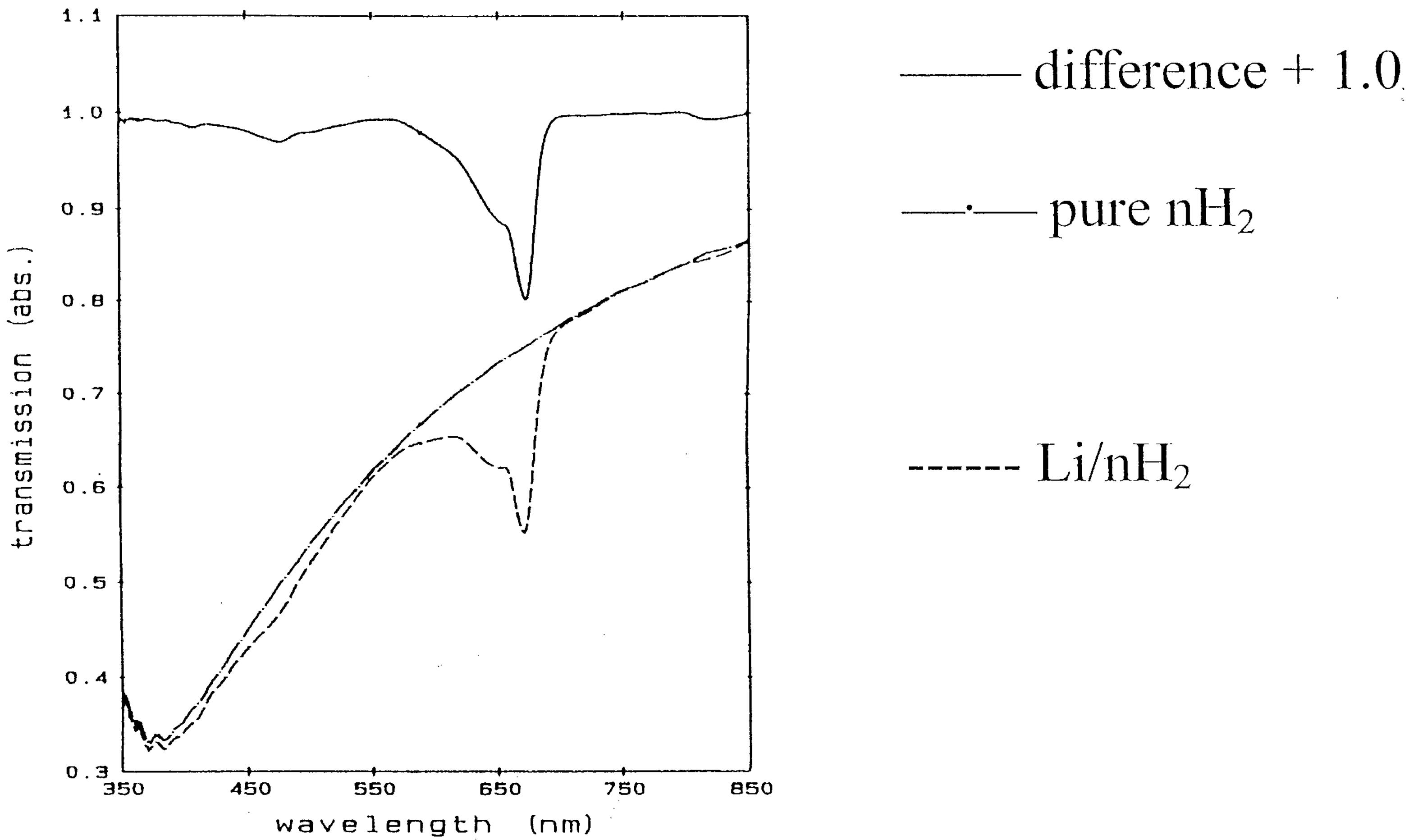
[b] Private communication.

[c] Fontana, B. J. (1959). *J. Chem. Phys.* **31**, 148.

* Difficult to distinguish energy release by small concentrations of very energetic species vs. low energy re-arrangements of host.

[A.M. Bass and H.P. Broida, "Formation and Trapping of Free Radicals" (Academic, New York, 1960)]

Transmission Spectrum of Li/nH$_2$, d ≈ 10 μ



M.E. Fajardo, J. Chem. Phys. **98**, 110 (1993).

Optical Scattering in Solid Hydrogen

Crystal Growing and Quality (p. 81)

"There is a considerable art to growing hydrogen crystals of high quality. Good crystals are always grown slowly from the melt; a rapid freeze from the gas produces snow."

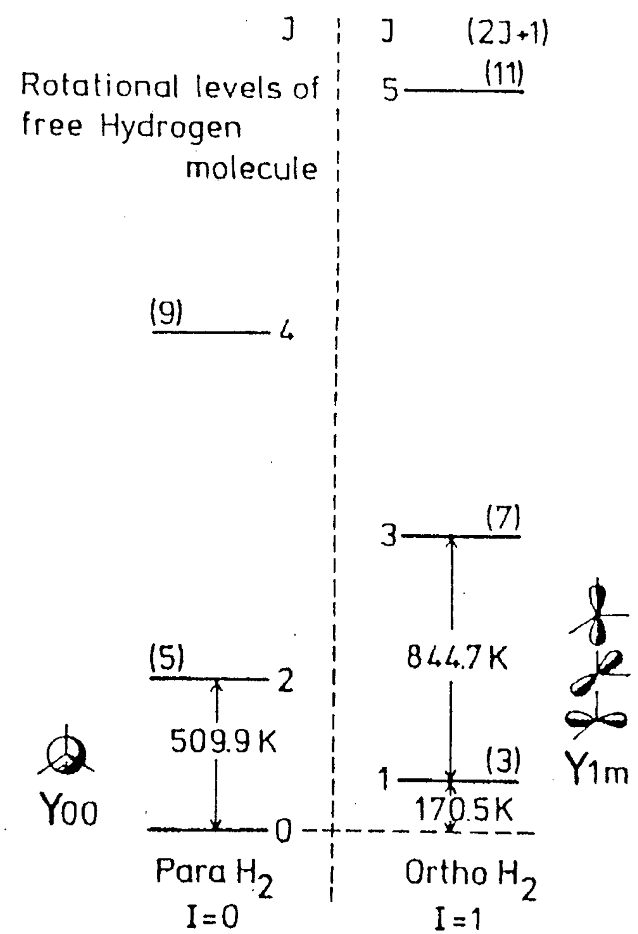
Crystallite Light Scattering (p. 83)

"The reason that a good hydrogen crystal is so hard to see is its low refractive index...an estimated 1.16!

Yet a 1 mm-thick layer of hydrogen crystallites can be a completely opaque brown-black."

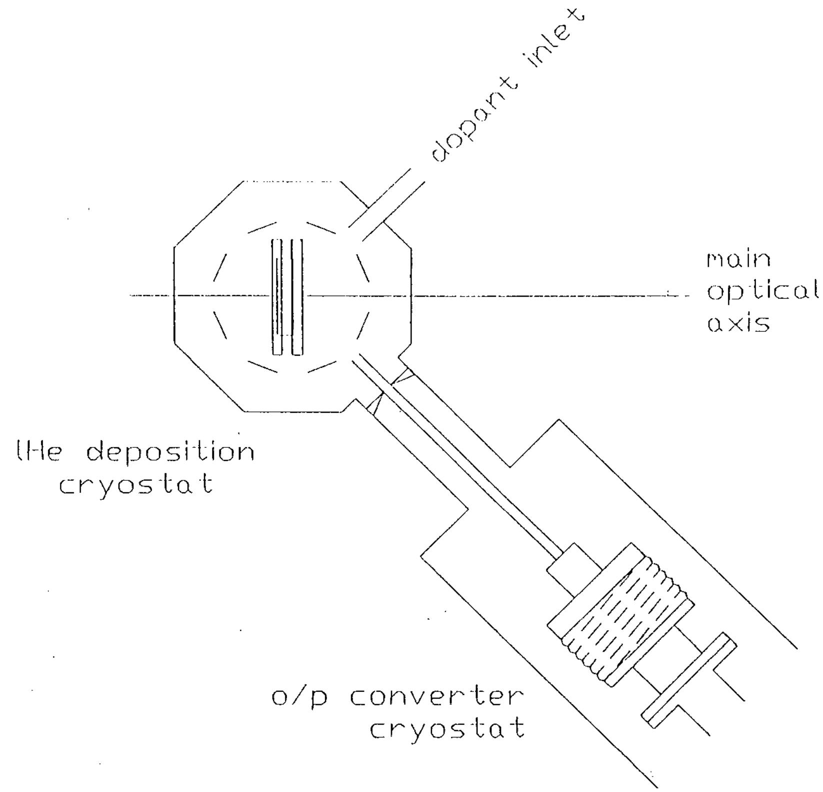
[P.C. Souers, Hydrogen Properties for Fusion Energy (UC Press, Berkeley, 1986)]

ortho- and para-hydrogen



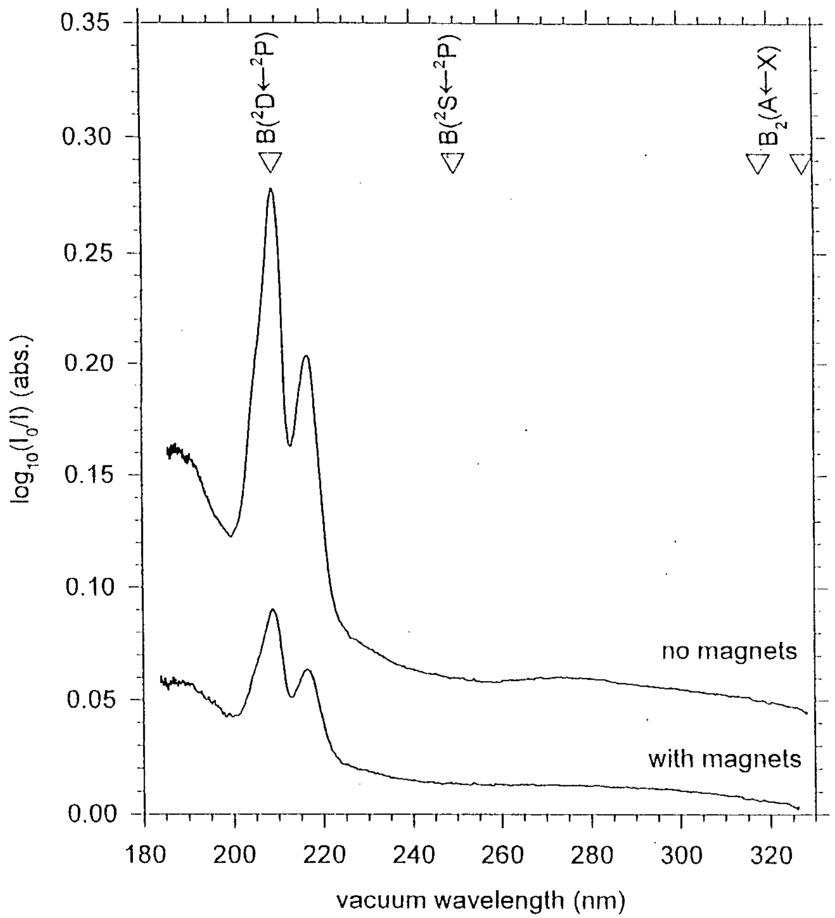
[I.F. Silvera, Rev. Mod. Phys. **52**, 393 (1980)]

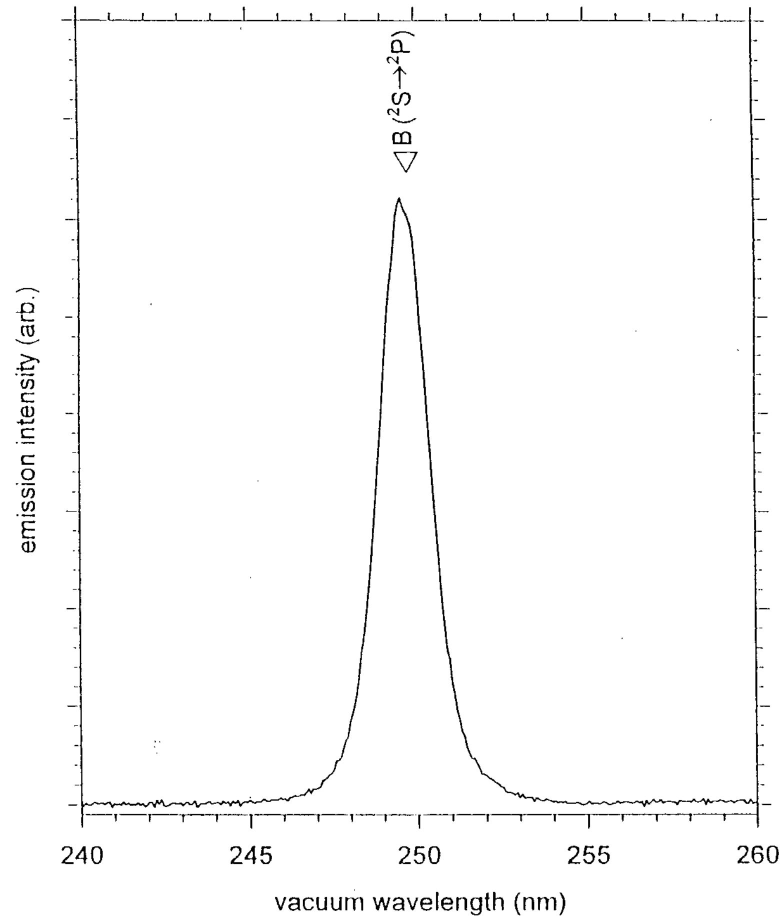
Rapid Vapor Deposition of Gram-Scale Optically Transparent pH_2 Solids (c1997)



M.E. Fajardo and S. Tam, J. Chem. Phys. **108**, 4237 (1998).
S. Tam and M.E. Fajardo, Rev. Sci. Instrum. **70**, 1926 (1999).

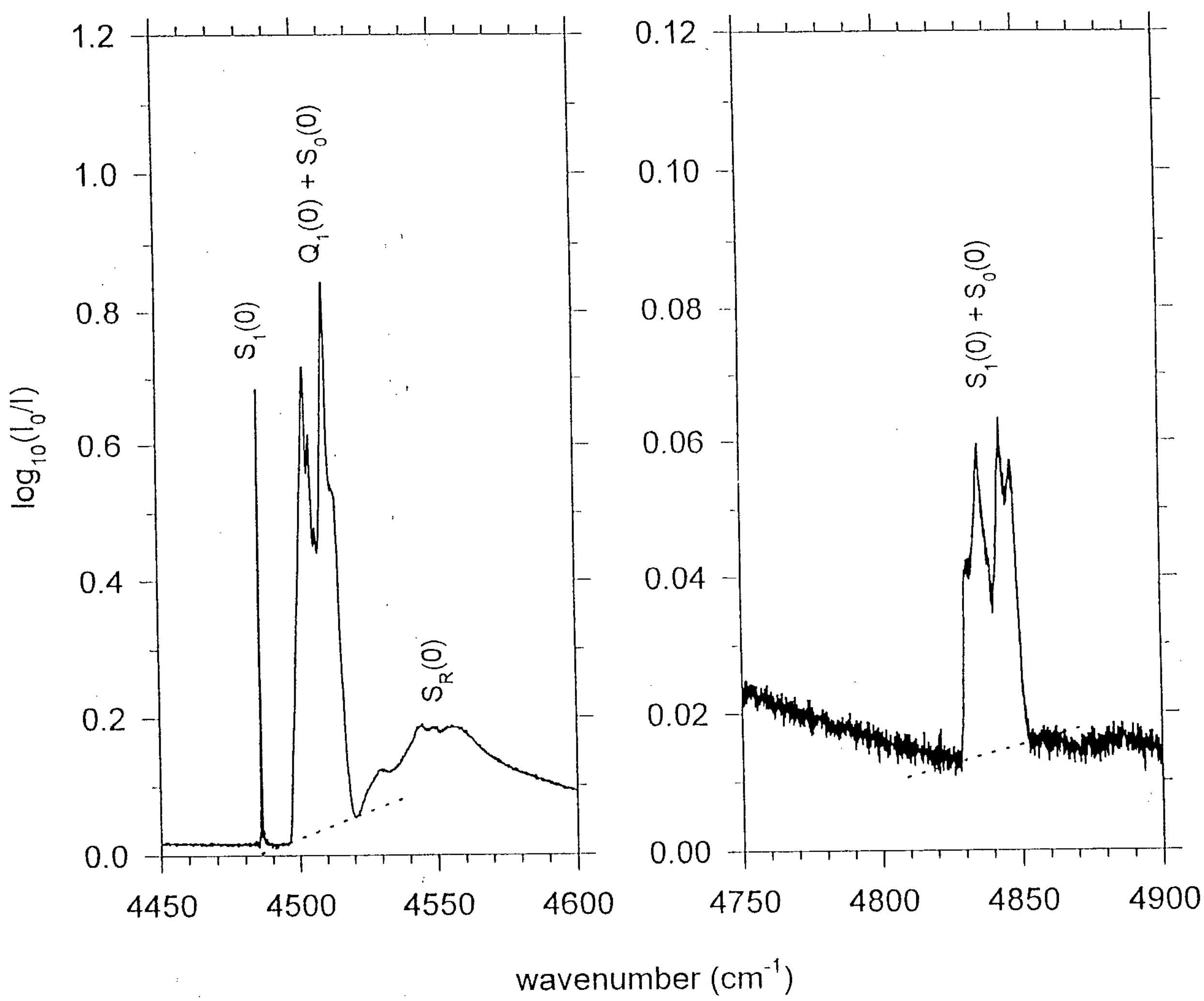
Electronic Spectroscopy of B/pH_2 ($d \approx 2$ mm)





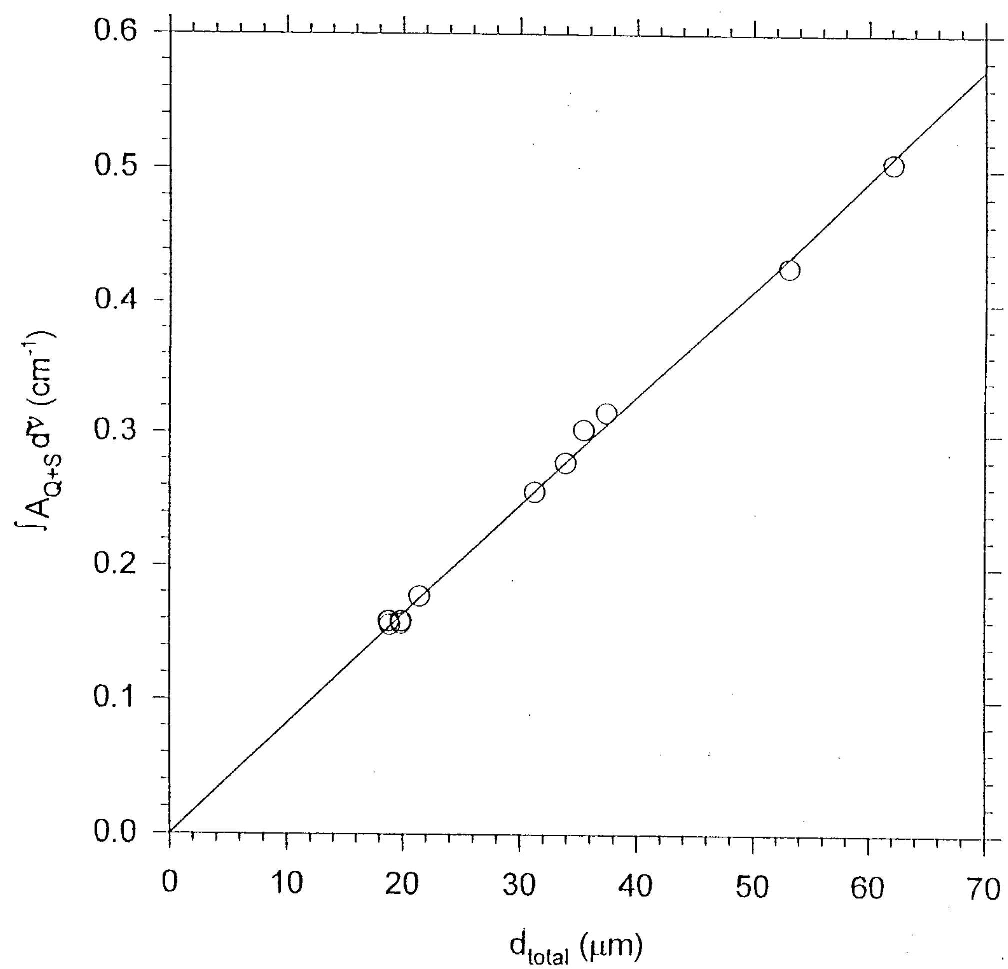
S. Tam, M. Macler, M.E. DeRose, and M.E. Fajardo, J. Chem. Phys. **113**, 9067 (2000).
[J.R. Krumrine, S. Jang, G.A. Voth, and M.H. Alexander, J. Chem. Phys. **113**, 9079 (2000)]

Solid pH_2 Thickness from IR Spectra



S. Tam and M.E. Fajardo, Rev. Sci. Instrum., submitted (2001).

Absorption Intensity vs. Thickness



new values:

$\int A_{Q+S}\, d\tilde{\nu} / d_{total} = 82 \pm 2$ cm^{-2}

$\int A_{S+S}\, d\tilde{\nu} / d_{total} = 6.3 \pm 0.3$ cm^{-2}

$\tilde{\alpha}_{Q+S} = 4.84(\pm 0.13) \times 10^{-14}$ cm^3/s

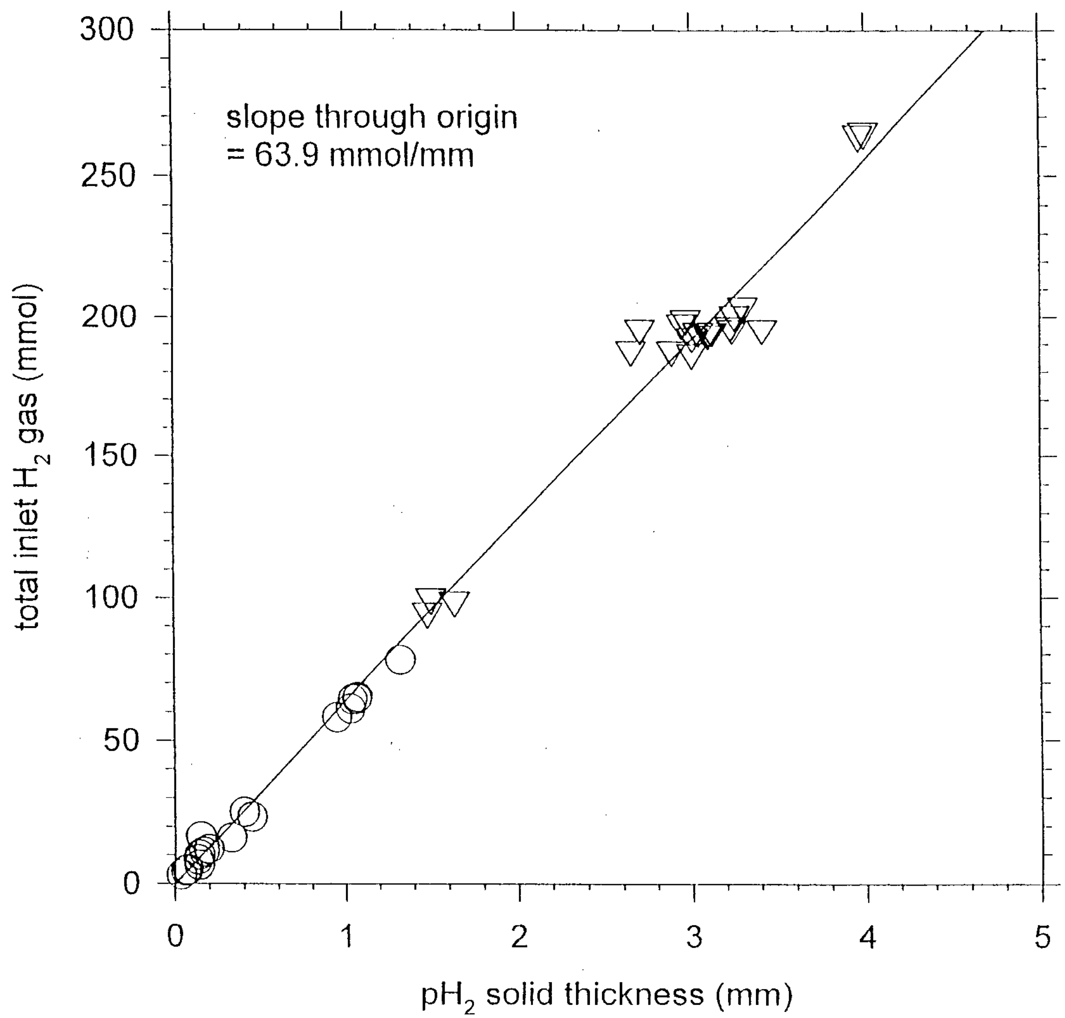
$\tilde{\alpha}_{S+S} = 0.35(\pm 0.02) \times 10^{-14}$ cm^3/s

literature (c1960):

$\tilde{\alpha}_{Q+S} = 4.5(\pm ?) \times 10^{-14}$ cm^3/s

S. Tam and M.E. Fajardo, Rev. Sci. Instrum., submitted (2001).

Constant pH_2 Deposition Efficiency



High Flux HEDM Sources

* Purchased commercial Al evaporator; PBN crucible holds $\approx$ 10 g Al in horizontal orientation.

* $T_{max} = 1200\ ^\circ C \Rightarrow P_{vap}(Al) \approx 8 \times 10^{-3}$ torr $\Rightarrow \Phi_{Al} \approx 10^{18}$ #/cm^2-s

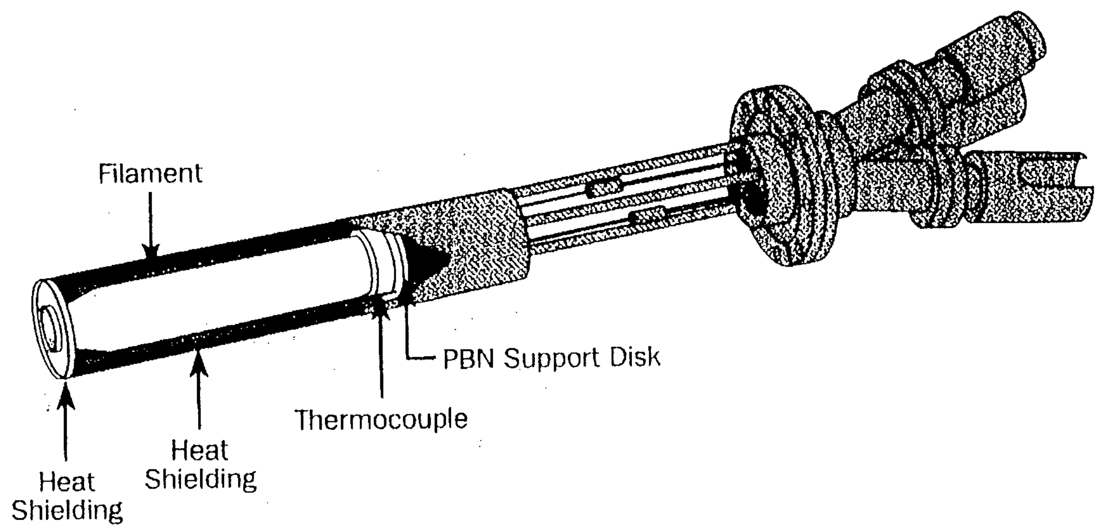
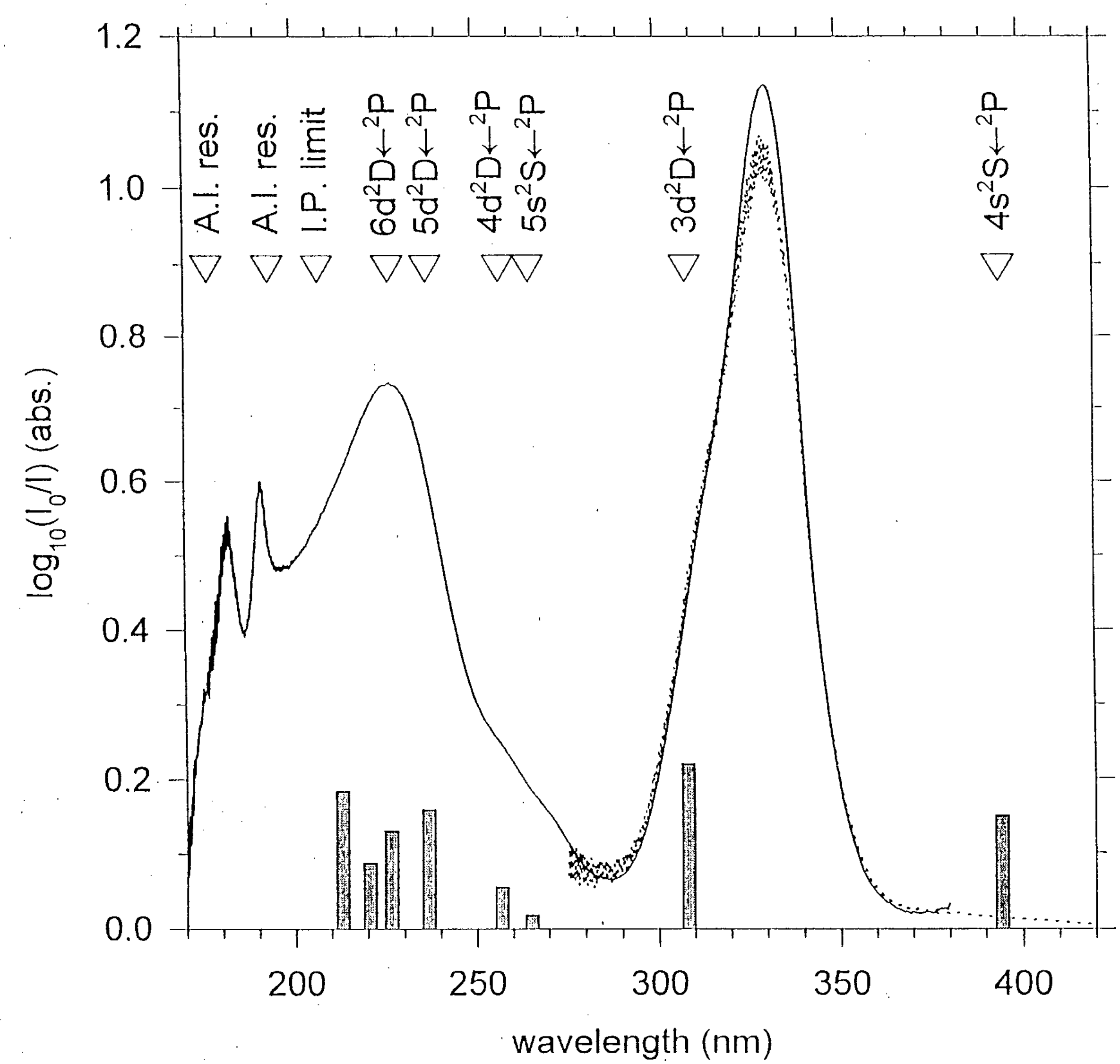
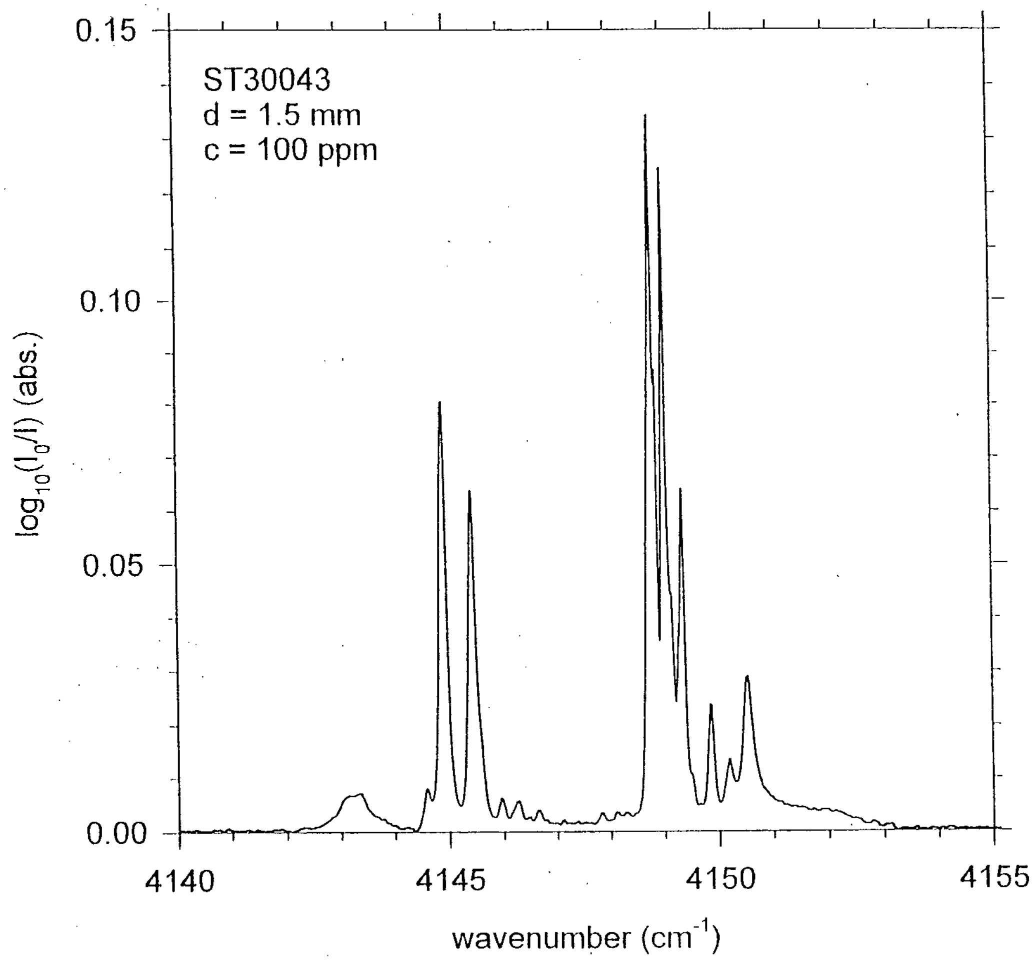


Figure 1-3: Schematic of the EPI SUMO™ Effusion Cell.

60 ppm Al/pH_2 UV Absorption (d=0.14 mm)

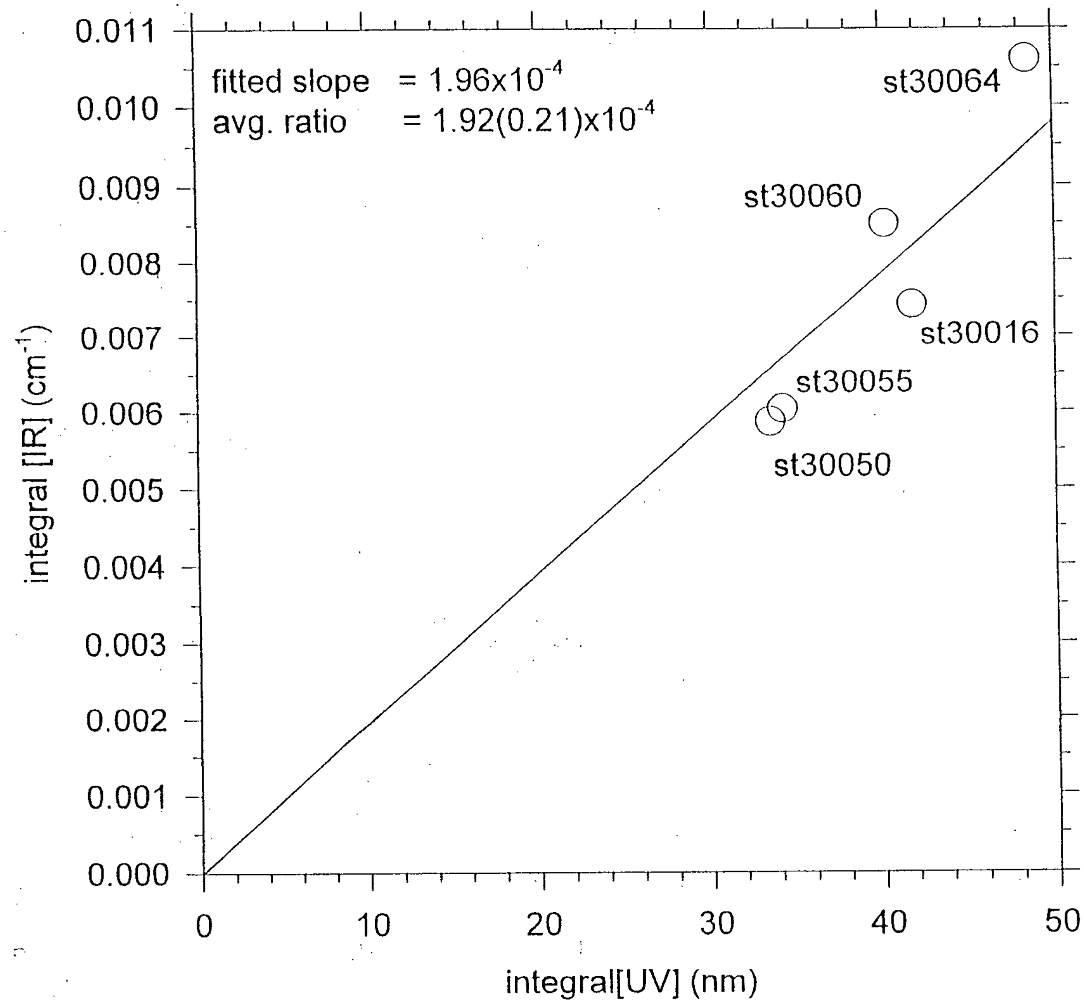


Al-induced IR Absorption Spectrum

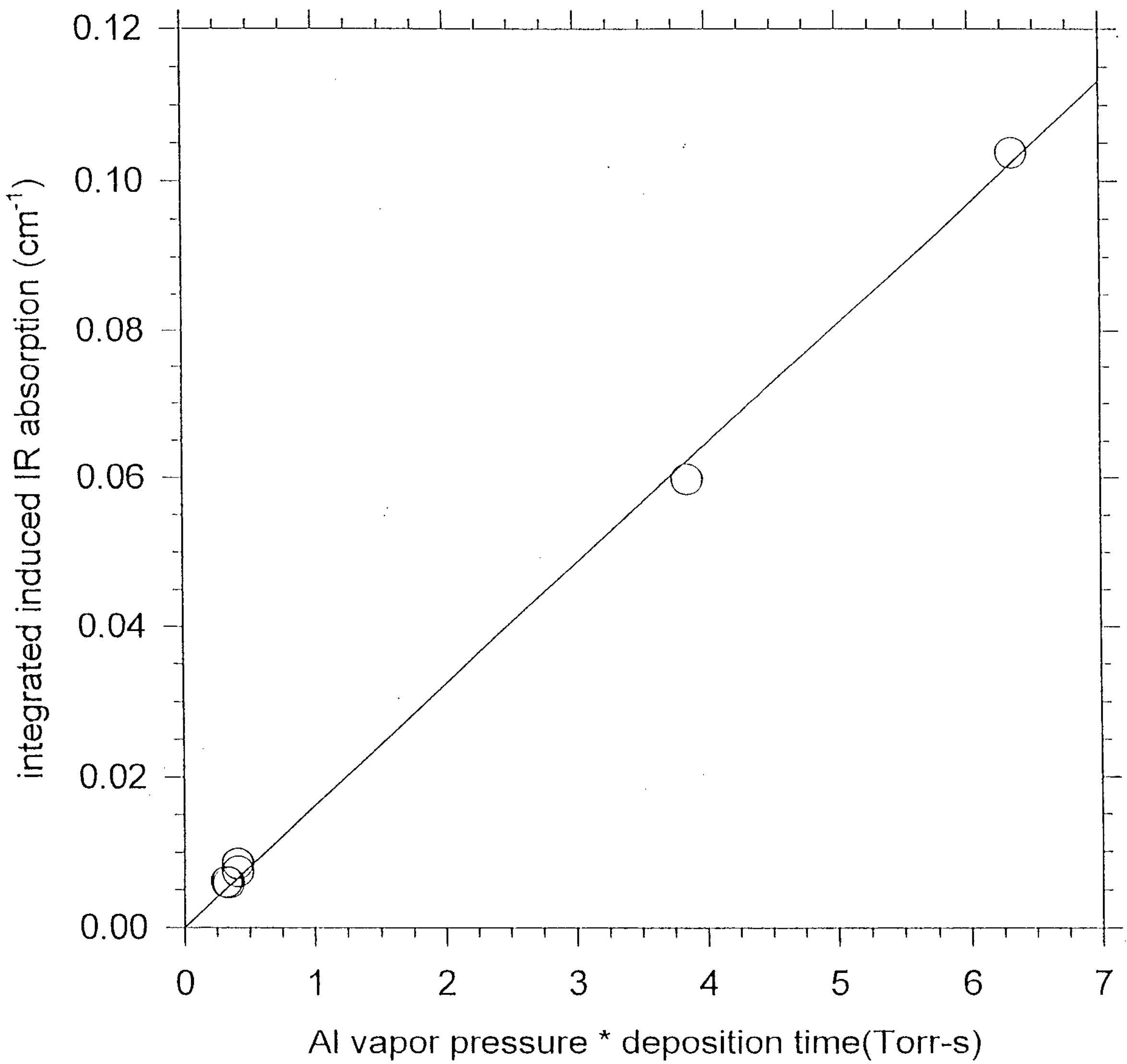


Analysis in collaboration with Prof. R.J. Hinde, U. Tennessee (Knoxville).

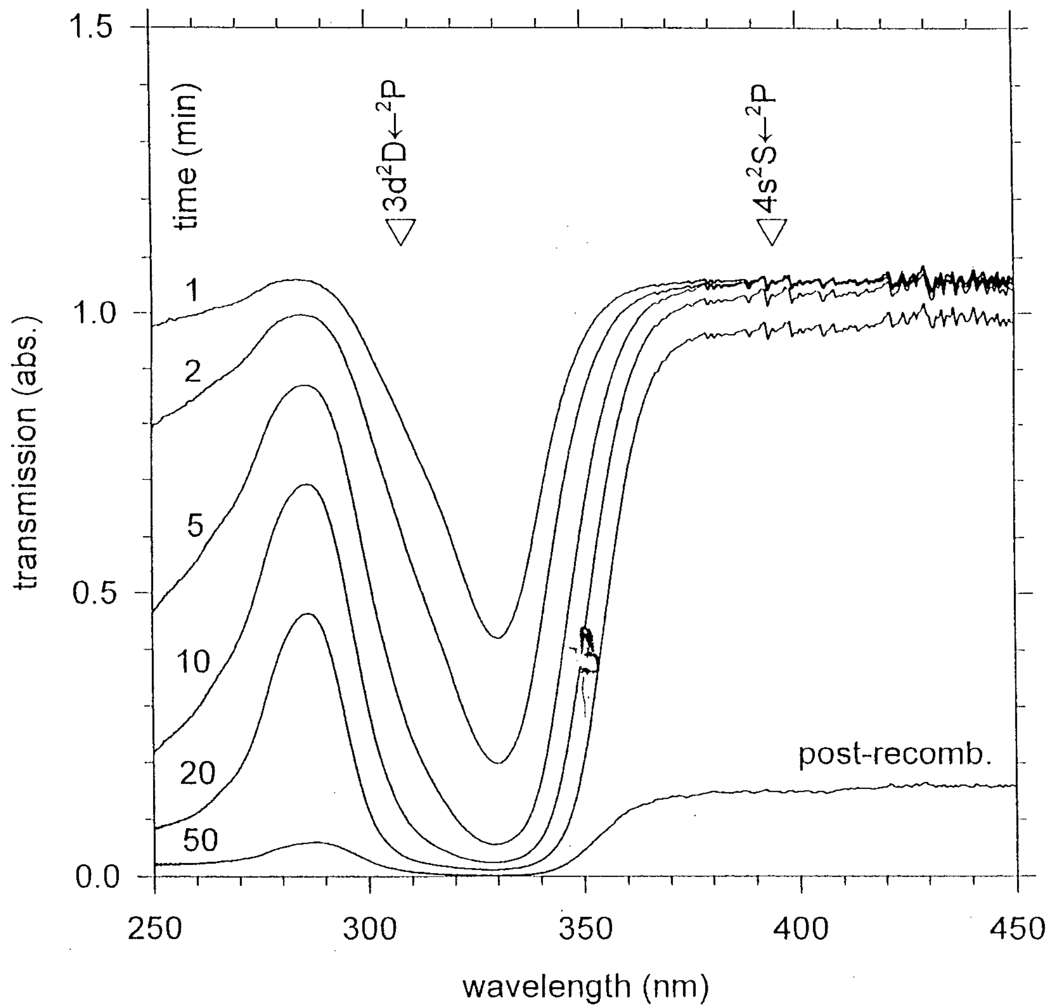
Correlation Between UV & IR Absorptions



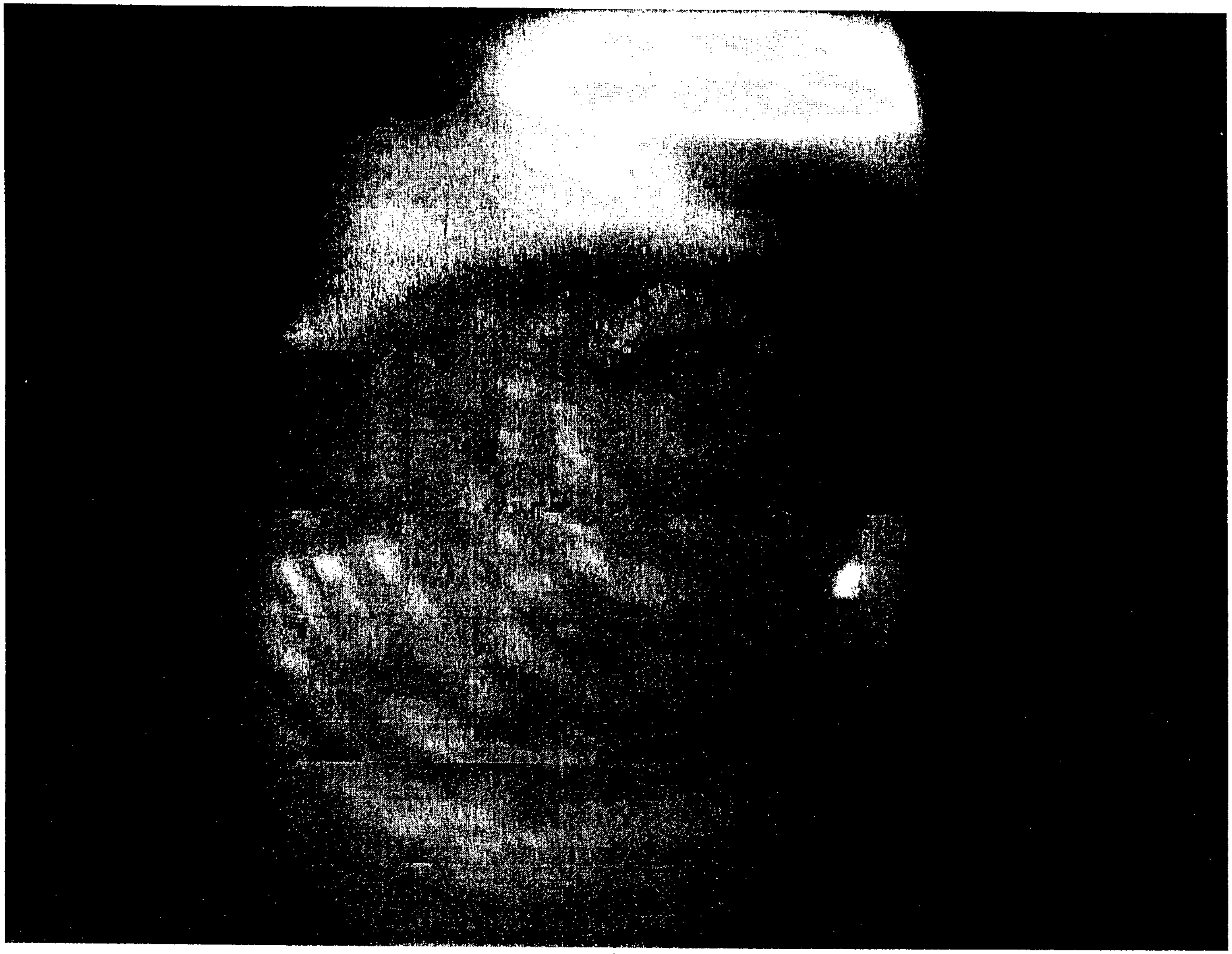
Constant Al Atom Deposition Efficiency



UV Spectrum of Recombined Al/pH_2

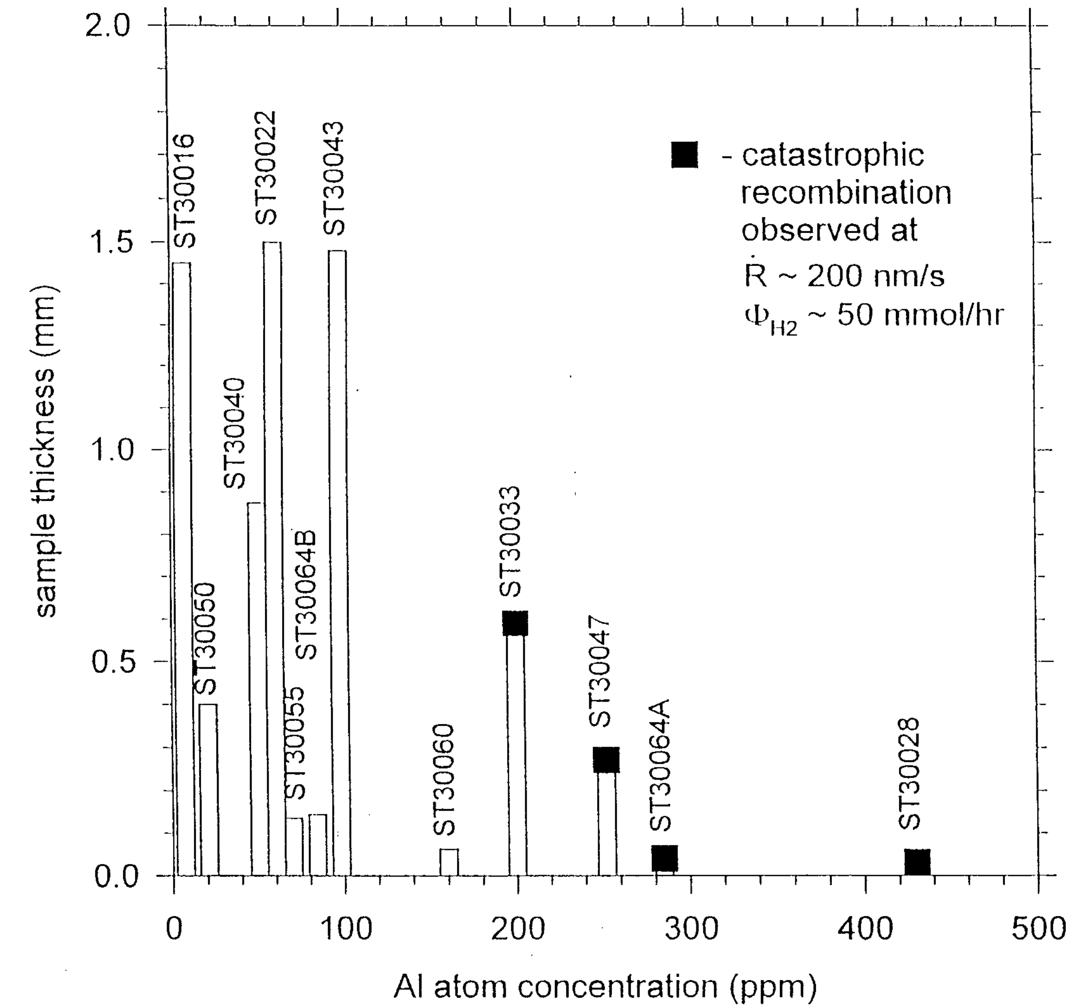


Recombination/reaction in Al/pH_2



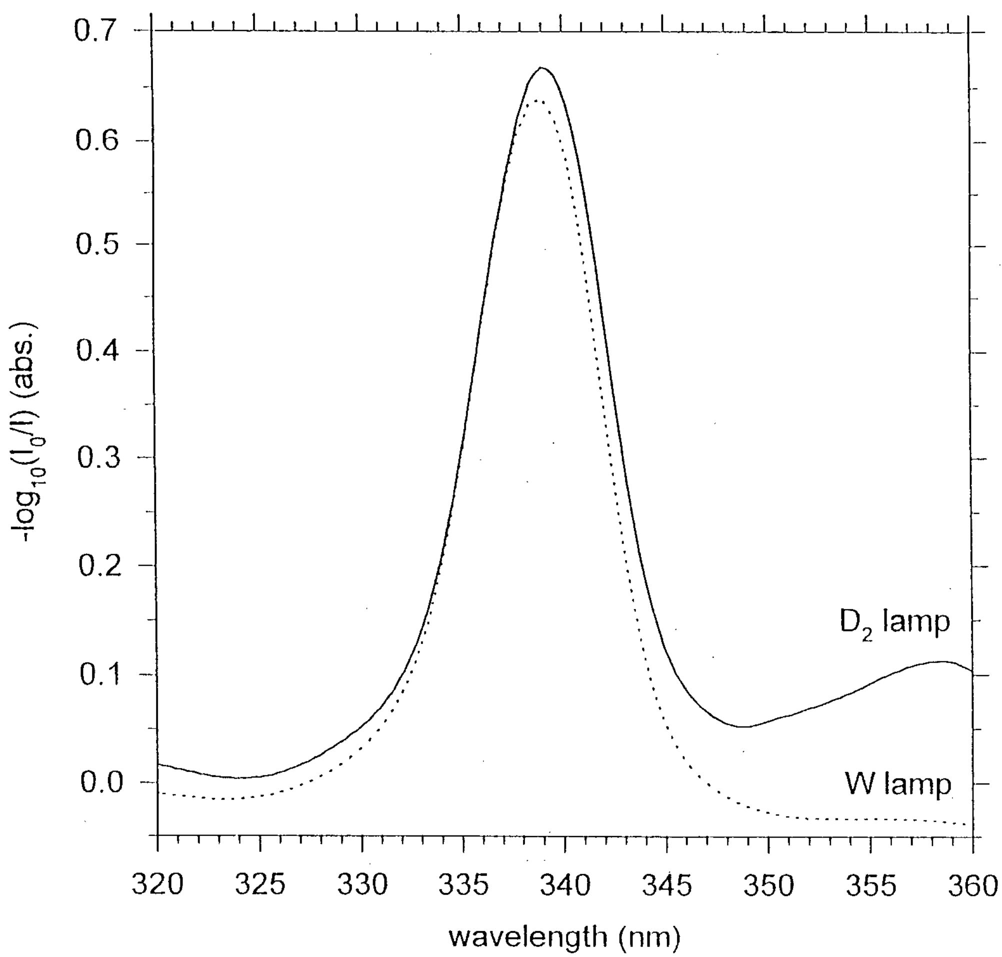
Summary of Al/pH$_2$ Deposition Results

OK, BOB?



1000 ppm Al/Ar

* Evaporate Al from 1 mm dia. Ta filaments



Al atoms in solid Ar

$$N_i = \frac{2.303\ m_e\, c^2 \int A_{10}\, d\lambda}{\pi\, e^2\, \lambda_0^2\, f_{ik}\, d}$$

$\int A_{10} d\lambda = 5.4$ nm

$d = 4\ \mu m$

$N_{Al} = 2.8 \times 10^{19}\ \#/cm^3$

$C_{Al} = 0.1\ \%$

$\Delta t = 13$ min

$\Phi_{Al} = 1.5 \times 10^{13}\ \#/cm^2\text{-s}$

@ R = 5 cm

Al/pH_2 Summary

* Demonstrated trapping of $\approx$ 0.1 % Al atoms in thin Ar solids using home-made Al atom source.

* Demonstrated Al-induced IR absorption by pH_2 molecules as a diagnostic of Al atom concentrations in high column density samples.

* Attempts (four to date) to exceed 0.02 % Al atom concentrations in thick pH_2 solids failed, resulting in catastrophic recombination (and reaction?) of the Al atoms.

* Interpretation: thick vapor deposited pH_2 solids impede dissipation of heat released upon atomic recombination, causing a recombination cascade. Attempt depositions of thin (~10 μm), high Al atom concentration Al/pH_2 samples (worked for Ar matrices).

Is Catastrophic Recombination Ubiquitous to Rapid Vapor Deposited pH_2 Solids?

* $$\frac{1}{k_{recomb}} = \frac{1}{k_{intrin}} + \frac{1}{k_{diff}}$$

* k_{intrin} depends on M-M interaction potential,
  increases with increasing well depth and range

* $\Rightarrow$ try Mg atoms as "HEDM" dopant
  Mg-Mg and Mg-Mg_n "van der Waals" interactions

[G.A. Voth, Quantum Simulations of Potential High Energy Density Materials, 1995 HEDM Conference Proceedings.]

M-M Diatomic Ground State Potentials

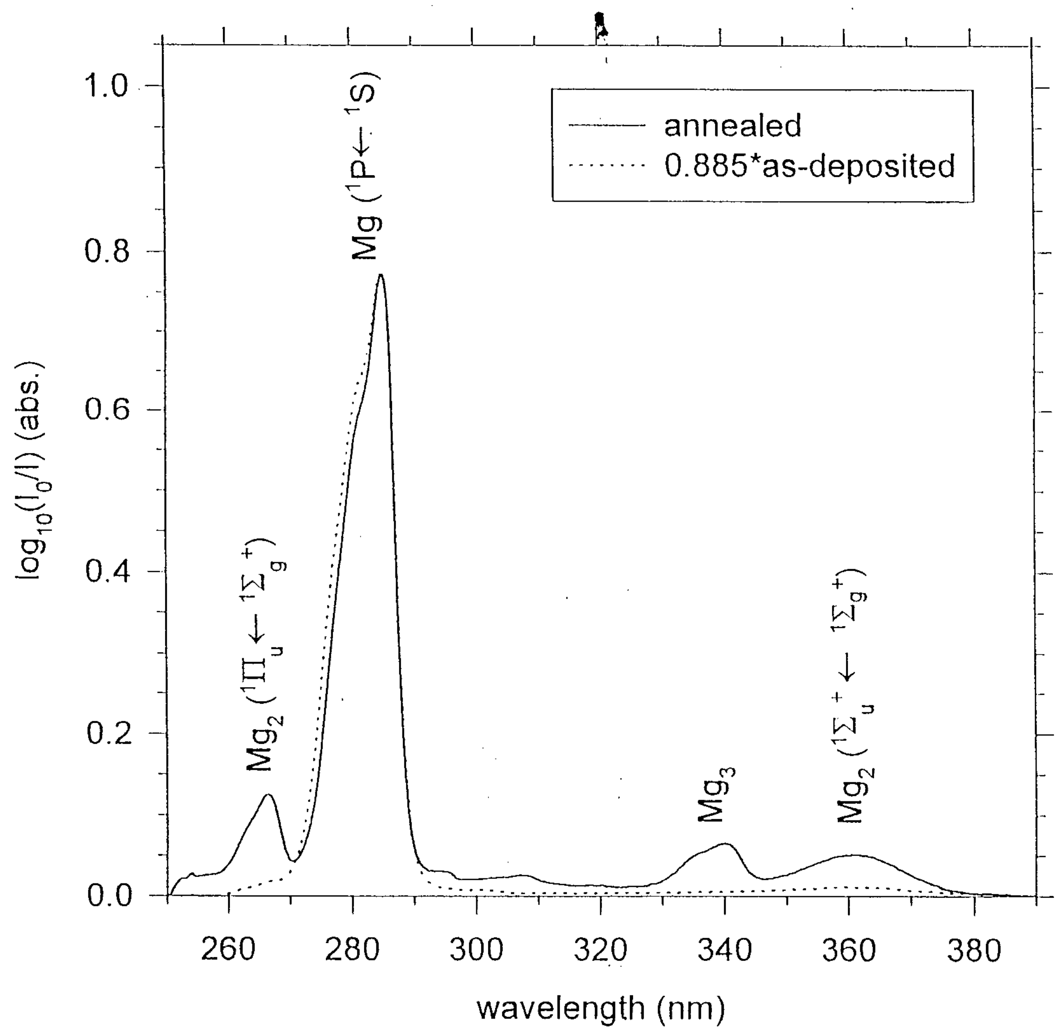
*****INCOMPLETE SLIDE*****

* Will make PLOT comparing Al-Al and Mg-Mg ground state potentials, <u>available from open literature</u>.

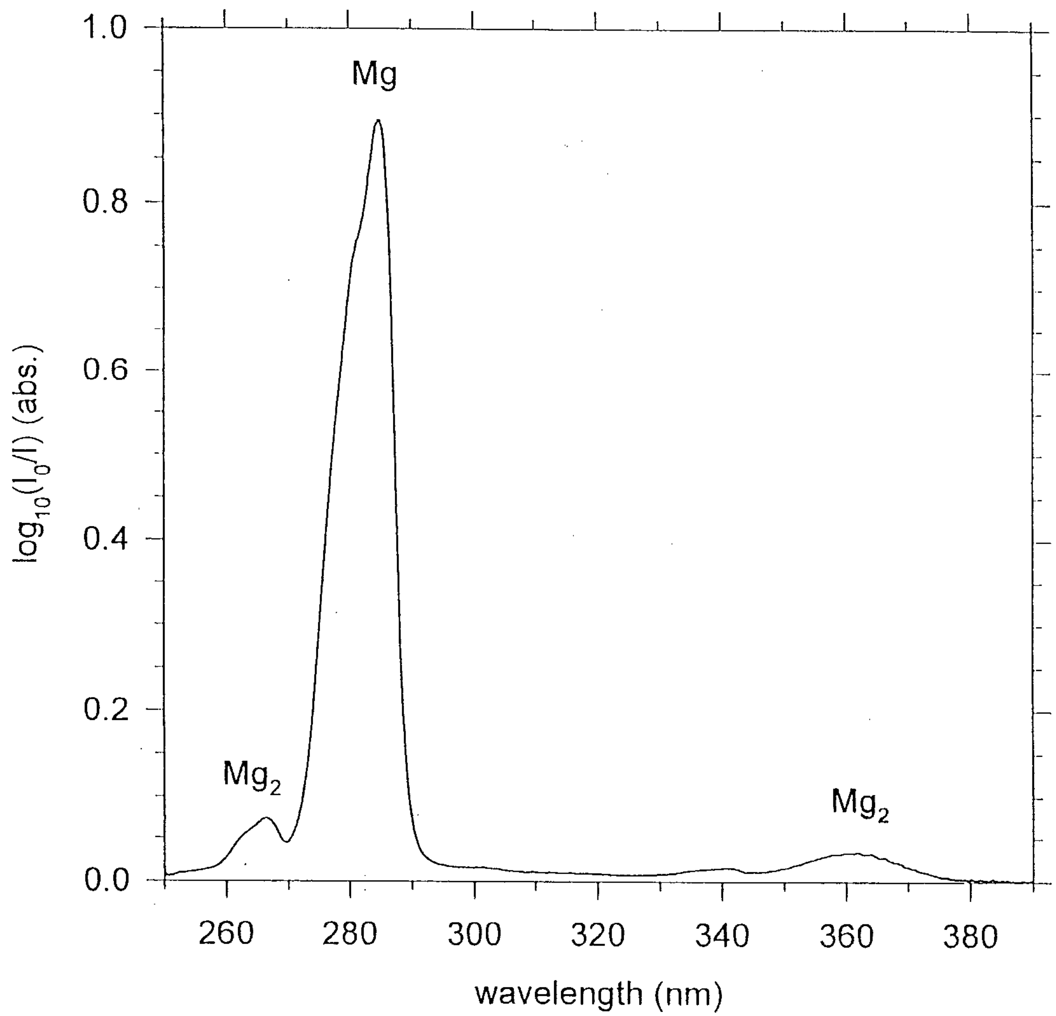
* if not too cluttered, include Li-Li, B-B potentials, too.

* shallower wells and especially weaker long-range interactions mean reduced intrinsic recombination rates, according to G. Voth.

Annealing of 10 ppm Mg/pH_2 (d=0.07 mm)



As-Deposited 35 ppm Mg/pH_2 (d=0.02 mm)



Contractor Support of In-House Effort

* Assignment of Al/pH_2 UV absorptions.
can change calculated Al atom concentrations by factor of 2!

* Modeling of Al atom induced IR absorptions

* Modeling of Mg recombination in solid pH_2 (?)

* Open Discussion:
coordination of efforts
other suggestions?

Recommendations for Future Experiments

* In-House:

  Complete Al/pH_2 and Mg/pH_2 experiments

  Compare Al vs. Mg to test effects of k_{intrin}

  Vary pH_2 deposition rate/sample thickness , and compare with Ne and Ar hosts to test k_{diff}

  Evaluate feasibility of rapid vapor deposition method

  Thermal B atom source SBIR project underway (B. Larson)

* AFOSR Contractors:

  Cluster Pickup and Deposition

  Deposition Directly onto lHe II (ala Gordon)

  In-Situ Photolysis of HEDM Precursors (Apkarian, Stwalley)

  Open Discussion: other suggestions?

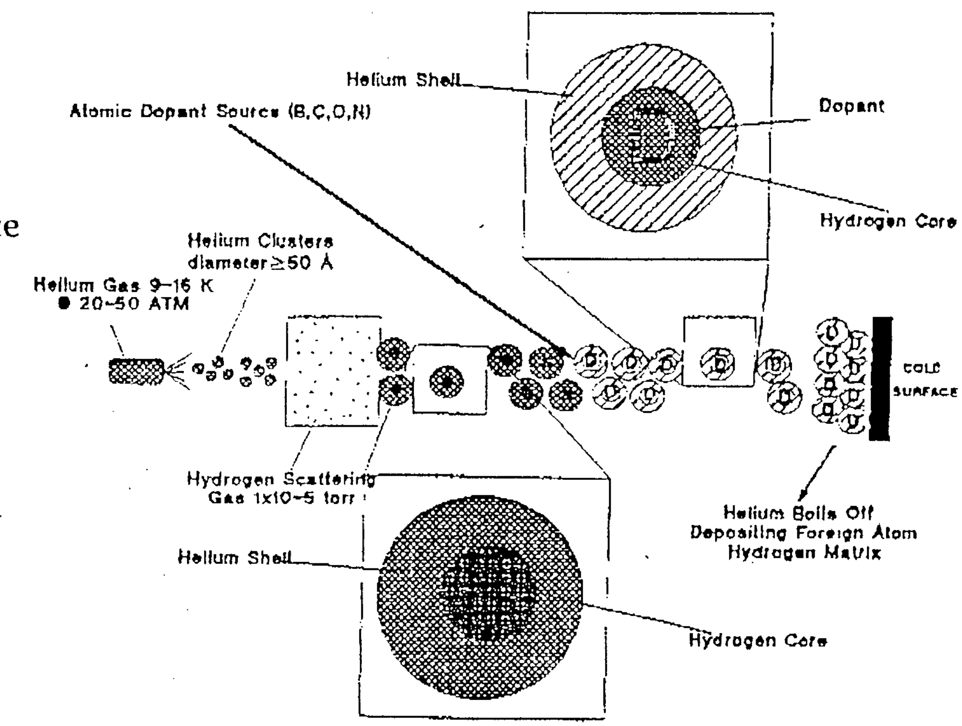
Future Direction: Cluster Deposition (?)

Toward the Production of Measurable
Quantities of Highly Doped Solid Hydrogen

High Energy Density Matter Contractors Conference
June 4-7, 1995

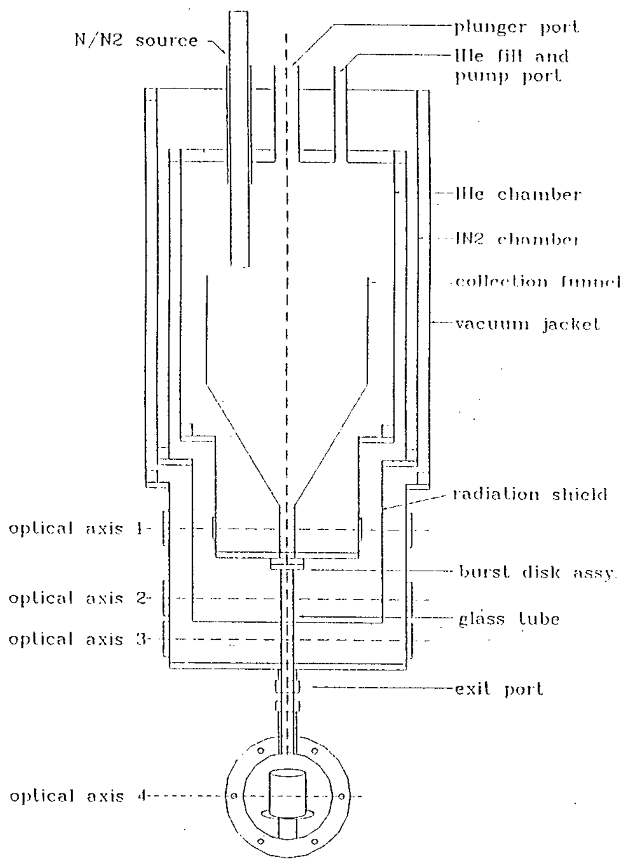
Berton Callicoatt, Kenneth C Janda, V. A. Apkarian, R. B. Gerber
Zhiming Li, P. Taborek and J. Rutledge
Advanced Cryogenic Materials Group
University of California
Irvine, California

The goal of this effort is to produce measurable quantities of highly doped (5-10%) solid hydrogen. The desired dopant atoms are C, B, O, and N. Our approach to this material is via the cluster deposition technique, as illustrated in Figure 1. First, a beam of large He clusters (between 10^4 and 10^5 He atoms per cluster) is created following the methods of Toennies[1] and Scoles.[2] Next, the He clusters are passed through a scattering chamber that contains hydrogen molecules and, in the process, "pick-up" between 12 and 20 hydrogen molecules. During the pick up process, sufficient He atoms evaporate for the cluster to maintain a temperature of about 1 K, and the hydrogen is expected to make a small micro-crystal within the He cluster. Next, the He cluster picks up the desired dopant atom. Again, He atoms evaporate to cool the cluster back to 1 K.



- * Most excess heat is dissipated before the clusters are deposited.
- * Chance to beat the "statistical limit" of stored atom concentration.
- * Either higher fluxes or UHV deposition environment required.

Future Direction: Deposition onto lHe II (?)



Based on E.B. Gordon's work

"Big-Flush" (c1995)

CESE discharge of N_2/He

Optical emission was only diagnostic (N/D_2 samples didn't glow!)

Need alternative (species specific) experimental diagnostics: ESR, NMR, FIR absorption… (?)

Future Direction: In-Situ Photolysis (?)

* V.A. Apkarian, et al. experiments (c1994):

$$O_2/D_2 + h_\nu \rightarrow O/D_2 + ?$$

(5% $O/H_2 \Rightarrow$ 25s (6%) I_{sp} improvement, so Al > O > H)
UV induced desorption of H_2O inside vacuum chamber complicates monitoring $O + H_2$ reactions.

* W.C. Stwalley proposal (c1992):

$$\begin{aligned}
M + h_\nu &\rightarrow M^* \\
M^* + H_2 &\rightarrow MH + H \\
MH + h_\nu' &\rightarrow M^* + H(\text{cold}) \\
M^* &\underline{\rightarrow} M + h_\nu'' \\
H_2 + h_\nu + h_\nu' &\rightarrow 2H + h_\nu'' \text{ (net reaction)}
\end{aligned}$$

Experimental Admonitions

* Must work with hydrogen! Some efforts on model systems are fine, but results may not generalize cleanly to hydrogen.

* Must focus on production and quantitative measurement of ~ 1 % concentrations of energetic species in solid hydrogen. Species specific diagnostics are preferred.

* Worry about scaling up later, must demonstrate progress towards larger concentrations to maintain viability of Cryosolid Propellants Task.